[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

THE EFFECT OF CONFIGURATION OF CERTAIN UNSATURATED 1,4-DIKETONES ON ADDITION-CYCLIZATION REACTIVITY

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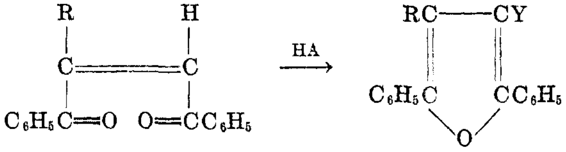
Received June 30, 1953

It has been observed that certain *cis* dibenzoylethylenes are more easily furanized by acidic reagents (HA) than are the corresponding *trans* isomers even though in certain cases the *cis* isomers are known to be the stable rather than the labile forms (1, 2). As examples, *cis*-chlorodibenzoylethylene (I, R = Cl) reacts with the acetic anhydride-sulfuric acid reagent to give the acetoxy furan (II: R = Cl, Y = $OCOCH_3$), and with acetyl chloride and sulfuric acid to give the 3,4-dichlorofuran (II: R = Cl, Y = Cl), whereas under the same conditions the *trans* isomer failed to react. *Cis*-methyldibenzoylethylene (I: R = CH_3), but not the labile *trans* isomer, reacted with acetic anhydride-sulfuric acid to give the acetoxyfuran (II: R = CH_3, Y = $OCOCH_3$).

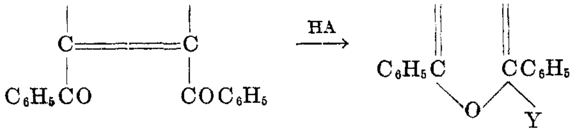


I II

This same pattern of relative reactivities has now been observed in the case of the dibenzoylstyrenes where the stable *cis* isomer (I: R = C_6H_5) but not the labile *trans* isomer, reacts in the cold with acetic anhydride-sulfuric acid to give the acetoxyfuran (II: R = C_6H_5, Y = $OCOCH_3$).

It was hoped that hydrogen bromide in acetic acid or anhydride might be used also to distinguish between the *cis* and *trans* isomers, but in this case both isomers readily gave the furan. In view of the facility of the *trans* to *cis* rearrangement by acids, it is probable that here isomerization occurs first and that the labile *trans* form does not react directly in the furanization reaction.

Cis disubstituted dibenzoylethylenes (III), which cannot go to true furans (except by reduction) because of the lack of an ethylenic hydrogen, undergo facile acid catalyzed addition-cyclization to hydroxyfuranone types (IV) (2).



III IV

(a) R = CH_3 (c) HA = $Ac_2O—H_2SO_4$ (f) Y = $OCOCH_3$

(b) R = C_6H_5 (d) HA = $HCl—CH_3OH$ (g) Y = OCH_3

(e) HA = $AcCl—H_2SO_4$ (h) Y = Cl

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We now report one case, bromodibenzoylstyrene (IIIb), where the stable *trans* isomer has been obtained from the labile *cis* isomer by the action of sunlight on an acetone solution with or without a trace of iodine as a catalyst. The configurations follow from the synthesis of the *cis* isomer by nitric-acetic acid oxidation of the corresponding furan. Both stereoisomers are shown by their ultraviolet absorption spectra to be essentially unsaturated 1,4-diketones although the conjugated systems must be far from planar because of the very considerable mutual steric interferences by the four substituents on the ethylenic linkage. In neither isomer does the 2-phenyl appear to enter into effective chalcone (benzalacetophenone) type conjugation (*cf.* 3).

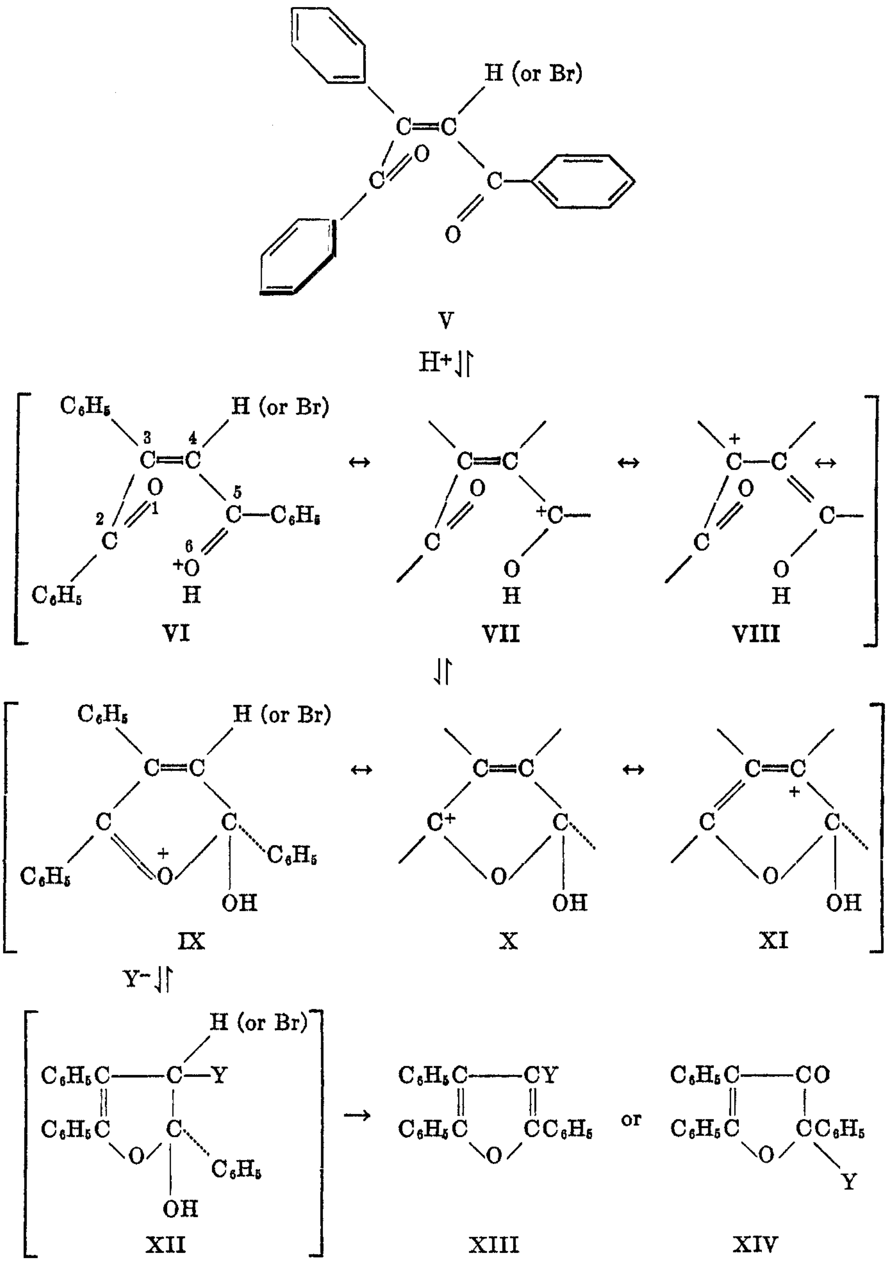
In this *cis-trans* pair there is found a sharp difference in reactivity; acetic anhydride and sulfuric acid readily convert the *cis* isomer to the furanone (IVb) (2), whereas under the same conditions the *trans* isomer is unaffected.

A similar difference in reactivities seems to exist in the case of the *cis* and *trans* dibenzoyldibromethylenes where under the same given conditions only the *cis* isomer reacts with acetic anhydride and sulfuric acid; but unfortunately the product of this reaction was not identified.

In this connection attention should be called to the remarkable case of one *cis-trans* pair, the dibenzoylchloroethylenes (I: R = Cl), where both of the two type reactions can be effected, furanization (4) and conversion to a furanone (5–7). In the addition of hydrogen chloride in 95% ethanol which gives the dichloro saturated diketone and the dichlorofuran, there is no evident distinction between the stereoisomers in respect to ratio and ease of addition-furanization (to II: R and Y = Cl); on the other hand both isomers are converted to the ethyoxyfuranone (IV: R = Cl, Y = OC_2H_5) when absolute ethanol is used as the solvent.

It is possible to explain the greater facility of the cyclization reactions of the *cis* isomers, where significant differences appear, in terms of reversible protonation of the oxygens of the α,β-unsaturated ketone systems present (V), and passage through the successive ionic transitions states VI–VIII and IX–XI which because of the resonance stabilization may be presumed to retain the configuration at the central ethylenic carbons. This is essentially a modification of the idea of a cyclic furanoid resonance-stabilized structure considered in earlier papers (2, 3).

One may assume that the two possible oxygen protonations (of which only that at the 4-carbonyl is illustrated) would be affected differently by the relative effectiveness of the conjugations involving the two carbonyl groups, and by the electrical effects of the substituents on the central ethylene linkage, but both would be involved in equilibrations. Presumably the protonation illustrated would be favored over that at the other non-coplanar 1-carbonyl because of the higher resonance stabilization expected in the ion (VI–VIII). However, regardless of the relative facility of protonation, as long as configuration is maintained in the protonated state, only in the *cis* compounds, and not in the *trans* could facile cyclization (ring-chain tautomerism or chelation) occur through XII to set in motion the formation of the furan or furanone (XIII or XIV). In the open-chain ion, VI–VIII, the system 3,4,5,6 would be closer to planarity than 1,2,3,4



when the 4-position carries hydrogen but would surely deviate considerably from planarity when the 4-position carries a substituent. The passage from the intermediate open-chain ion, VI–VIII, to the cyclic ion, IX–XI, must involve a steric eggbeater-like movement at the 2,3- and 4,5-bonds wherein the free non-coplanar and non-protonated carbonyl oxygen-1 in donating electrons to the carbonyl carbon-5 moves into the furan-oxygen position and becomes the furan oxygen, while simultaneously the protonated oxygen-5 moves away from the furan plane.

EXPERIMENTAL

Addition furanization of cis-dibenzoylstyrene (I: R = C_6H_5). A solution of 0.1 g. of the *cis* diketone in 20 ml. of acetic anhydride and 0.001 ml. of conc'd sulfuric acid was allowed to stand at 0° for 15 min. Hydrolysis gave 0.1 g. (90%) of the acetoxyfuran (II: R = C_6H_5, X = $OCOCH_3$). The *trans* isomer in an identical experiment was recovered unchanged.

A solution of 0.1 g. of the *cis* diketone in 10 ml. of conc'd acetic acid at 8° was treated with 1 ml. of 10% hydrogen bromide in acetic acid (3 min.). Addition of water precipitated 0.085 g. (87%; m.p. 123–127°) which was identified as the bromotriphenylfuran. Similar results were obtained using the *trans* isomer. Similar reactions with both isomers using acetic anhydride as the solvent at 0–3°, led to recovery of starting materials.

trans-Bromodibenzoylstyrene, $C_6H_5COC(Br){=}C(C_6H_5)COC_6H_5$. A solution of 0.1 g. of the *cis* isomer (IIIb) in 3 ml. of acetone with or without enough added iodine to impart permanent color, was exposed to bright sunlight for 1.5 to 2 hours. Evaporation and recrystallization from ethanol gave 0.065 g. (65%) of colorless crystals; m.p. 151–152°. Longer sunlight exposures led to increased amounts of non-crystalline products, and positive reactions for bromide ion could be obtained with alcoholic silver nitrate.

Anal. Calc'd for $C_{22}H_{15}BrO_2$: C, 67.53; H, 3.86.
Found: C, 67.60; H, 4.00.

As a check on the structure[2] of this compound, zinc and acetic acid *reductions of both the cis and trans isomers* were carried out and gave in each case mixtures of the saturated diketone $C_6H_5COCH_2CH(C_6H_5)COC_6H_5$, and 2,3,5-triphenylfuran.

The cis isomer (IIIb) upon reaction with 3:0.001 acetic anhydride-sulfuric acid mixture (3 min. at room temperature) gave the furanone (IVb, f) in 59% yield. The *trans* isomer in a similar experiment was recovered unchanged (84%).

cis-Dibenzoyldibromoethylene, $C_6H_5COCBr{=}CBrCOC_6H_5$, in reaction with 1:0.001 acetic anhydride-sulfuric acid mixture at 100° for 20 min. gave non-crystalline products. The *trans* isomer in a similar experiment was recovered unchanged (85%). At lower reaction temperatures both isomers were recovered unchanged.

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SUMMARY

In the several cases studied where differences exist, *cis* unsaturated 1,4-diketones, regardless of relative stability, are more readily converted than are their *trans* isomers into furans and furanones. This phenomenon has been explained in terms of retention of configuration in the active protonated transition states.

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[2] These experiments were carried out in this laboratory by C. L. Dickerson.